Electrodeposition of Pd based binary catalysts on Carbon paper via surface limited redox-replacement reaction for oxygen reduction reaction

Mmalewane Modibedi
mmodibedi@csir.co.za
Outline of the presentation

- Introduction:
  - Oxygen reduction reaction (ORR)
  - Fuel cells- Direct alcohol fuel cells (DAFC)

- Electrocatalysts:
  - Preparation
  - Characterisation
  - Electrochemical evaluation

- Conclusions

- Future Work
1. **Oxygen reduction reaction (ORR)**

- ORR is most important reaction in life processes and energy converting systems: **Fuel cells**, Sensors

- ORR pathways in aqueous acidic solution:

\[
\begin{align*}
\text{O}_2 & \quad \xrightarrow{2 \text{ e}^-} \quad \text{H}_2\text{O}_2 \\
E_0 &= 0.70 \text{ V} \\
\text{H}_2\text{O}_2 & \quad \xrightarrow{2 \text{ e}^-} \quad \text{H}_2\text{O} \\
E_0 &= 1.76 \text{ V} \\
4 \text{ e}^- & \quad \quad \\
E_0 &= 1.229 \text{ V}
\end{align*}
\]

*Preferred pathway for FC application: 4e-*
1. ORR Catalysts

Oxygen reduction activity on various transition metal electrodes as a function of the oxygen binding energy from DFT calculations.

2. Direct Alcohol Fuel Cells

CHALLENGES:

• Sluggish reaction: better performing ORR catalyst
• High cost of catalyst: reduce amount of Pt, alternative catalysts
• Alcohol crossover: alcohol tolerant catalyst
3. **Electrocatalysts**

3.1.1 **Electrochemical atomic layer technique (ECALD):**

**Definition:**
alternated electrodeposition of atomic layers of elements on a substrate, employing under-potential deposition (UPD) in which one element deposits onto another element at a voltage prior to that necessary to deposit the element onto itself

**Advantages:**
- ambient temperature,
- use small concentrations of precursor solutions,
- optimized solutions and potential separately

Offers **atomic layer control** - fundamental for controlled growth processes

Sequential electrodeposition coupled to Surface-limited Redox-replacement reactions: Synthesis of multilayered Pt electrocatalyst

1. Clean substrate with blank electrolyte (BE); Inject Cu$^{2+}$ solution at $E >> E_{Cu-Cu^{2+}}$

2. Potentiostatic electrodeposition at $E_{dep} > E_{Cu-Cu^{2+}}$ (Underpotential Deposition (UPD)) or $E_{dep} < E_{Cu-Cu^{2+}}$ (small OverPotential Deposition (OPD)) - to produce sacrificial Cu adlayer on active sites of the substrate; Rinse with BE

3. Inject H$_2$PtCl$_6$ solution and allow surface-limited redox-replacement (SLRR) of Cu by Pt at open circuit (OC)

4. Pt nanodeposit on substrate; Rinse with BE and inject Cu$^{2+}$ solution at $E >> E_{Cu-Cu^{2+}}$

5. Potentiostatic electrodeposition at $E_{dep}$ to produce sacrificial Cu adlayer on active sites on Pt adlayers; Rinse with BE

6. Inject H$_2$PtCl$_6$ solution and allow surface-limited redox-replacement (SLRR) of Cu by Pt at OC
3.1.1 ECALD cont’d:

**Noble-Metal:** Pt, Pd (more abundant and cheaper than Pt)

1mM PdCl₂ + Chloride as complexing agent
LB Sheridan et al., Langmuir 29 (2013) 1592

**Substrate:** Fuel Cell Carbon paper
- small OPD

**Repeat cycles:** Optimal 8X- monometal, Pd₈Pt₈, Pt₈Pd₈, Pd₁₆Pt₁₆, Pt₁₆Pd₁₆, Pd₁₆Pt₈
16 PdPt co-deposition

Modibedi et al., *ECS Trans.* 50 (21) 2013
Modibedi et al., *Electrochim.Acta* 128 2014
1. Rinse cell with BE at 0.2V, rinse with Cu$^{2+}$ solution
2. Cu deposition at -0.05V, rinse with BE at -0.05V
3. Rinse with Pd$^{2+}$ solution at OCP, SLRR at OCP
PdPt: Morphology and electrochemical evaluation

(i) 0.1 M HClO4 + N2

(ii) 0.1 M HClO4 + O2

(iii) Current-Potential curves
PtPd: Morphology and electrochemical evaluation

(i) 0.1 M HClO₄ + N₂

(ii) 0.1 M HClO₄ + O₂

(iii) Current-Potential curves
PdPt: Morphology and electrochemical evaluation

(i) 0.1 M HClO4 + N₂

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(i) 0.1 M HClO4 + N₂

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(iii) Current-Potential curves
## Conclusions

<table>
<thead>
<tr>
<th>Electro-Catalyst</th>
<th>Onset potential (V) vs Ag/AgCl</th>
<th>Max. current density (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd 8x</td>
<td>0.504</td>
<td>0.5415</td>
</tr>
<tr>
<td>Pt 8x</td>
<td>0.548</td>
<td>0.2892</td>
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<tr>
<td>Pd8Pt8</td>
<td>0.546</td>
<td>0.6123</td>
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<tr>
<td>Pt8Pd8</td>
<td>0.584</td>
<td>0.6369</td>
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<tr>
<td>Pd16Pt16</td>
<td>0.582</td>
<td>0.8801</td>
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<tr>
<td>Pt16Pd16</td>
<td>0.725</td>
<td>1.3538</td>
</tr>
<tr>
<td>Pd16Pt8</td>
<td>0.581</td>
<td>1.2431</td>
</tr>
<tr>
<td>16 PdPt* co-deposition</td>
<td>0.566</td>
<td>1.3477</td>
</tr>
</tbody>
</table>

- Different structural shapes were observed - sequence
Future Work

• Investigate catalyst tolerance to alcohol (methanol, ethanol)

• Optimization of Pd: Pt ratio that will give same or better performance than Pt

• MEA fabrication and FC testing under active conditions

• Explore the addition of 3rd metal to PdPt catalyst: Ni, Co
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